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THE "BASE-CATALYSED" FLUORINATION OF SO_2 BY XeF_2

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Summary

The fluorination of SO_2 by XeF_2 in the presence of compounds of the type MX (M = NMe_4, Cs, K; X = F, Cl) is described.

Reaction mechanisms are proposed in which the XeF_2 functions as a weak Lewis acid.

Introduction

The ability of acids to catalyse fluorination by kinetically "inert" XeF_2 has been observed in several systems. Thus I_2 [1], C_6H_6 [2] and SO_2 [1,3], which normally do not react with XeF_2, are readily converted to IF_5, C_6H_5F and SO_2F_2 respectively on addition of a trace of HF to the system. It has been suggested that the catalytic function of the acid is the removal of a fluoride ion from the XeF_2 with the formation of XeF^+, this being the reactive species.

The oxidation of I_2 to IF_5, which proceeds rapidly in the presence of HF, is prevented by the addition of CsF to the system, the acid presumably reacting preferentially with the "basic" CsF. The oxidation of SO_2 by XeF_2 might be expected to be similarly hindered by addition of base to the system. The following work, however, shows that this is not the case, and that salts such as CsF in fact promote the oxidation.

Results and discussion

XeF_2 was dissolved in SO_2 in the presence of the halides CsF, NMe_4F, KF, CsCl and NMe_4Cl. Experiments using XeF_2:halide ratios between 1:1 and 4:1 were carried out. The reaction products are summarised in Table 1.

The system NMe_4F–XeF_2–SO_2

On condensation of XeF_2 into a solution of NMe_4F in SO_2, heat was produced accompanied by gas evolution. Removal of the volatiles left a residue consisting of NMe_4SO_2F and lesser quantities of NMe_4SO_3F. The volatile products consisted of xenon and SO_2F_2 together with small amounts of SOF_2.

TABLE 1

Products of the reactions MX + XeF_2 + SO_2

MX	Solid products	Gaseous products
NMe_4F	NMe_4SO_2F; NMe_4SO_3F	SO_2F_2; SOF_2[a]; Xe
NMe_4Cl	NMe_4SO_2F; NMe_4SO_3F	SO_2F_2; SO_2FCl; SOF_2[a]; $S_2O_5F_2$[a]; Xe
CsF	$CsSO_3F$; $CsSO_2F$	SO_2F_2; SOF_2; $S_2O_5F_2$[a]; Xe
CsCl	$CsSO_3F$; $CsSO_2F$	SO_2F_2; SO_2FCl; SOF_2; $S_2O_5F_2$[a]; Xe
KF	KSO_3F; KSO_2F	SO_2F_2; SOF_2; Xe

[a] Trace quantities only.

A solution of NMe_4F in SO_2 contains discrete SO_2F^- ions. Removal of solvent from such a solution leaves the pure product NMe_4SO_2F [4].

To explain the above oxidation, it is proposed that the SO_2F^- ions initially form a weak complex with the XeF_2:

$$FSO_2^- + XeF_2 \rightarrow FS(O)OXeF_2^- \qquad (1)$$

which can easily lose a fluoride ion to form a second, also weak, complex:

$$FS(O)OXeF_2^- \rightarrow FS(O)OXeF + F^- \qquad (2)$$

The stability of a S^{IV}/Xe^{II} complex can be assumed to be low, and an intramolecular redox reaction, with the production of SO_2F_2 and xenon, is to be expected:

$$FS(O)OXeF \rightarrow SO_2F_2 + Xe \qquad (3)$$

The fluoride ions formed in reaction (2) would react with the solvent, producing further quantities of SO_2F^- ion.

The production of NMe_4SO_3F and SOF_2 is discussed under the CsF–XeF_2–SO_2 system.

The system NMe_4Cl–XeF_2–SO_2

A solution of NMe_4Cl in SO_2 reacted similarly to the previously described system. The solid products NMe_4SO_2F and NMe_4SO_3F were obtained in similar proportions to the above reactions. The volatile products consisted of substantial amounts of xenon, SO_2F_2 and SO_2FCl, together with traces of SOF_2 and $S_2O_5F_2$.

As above, weak intermediate complexes can be postulated whose decomposition would form the necessary products, the chloride, present in solution as the SO_2Cl^- ion, first forming an adduct with XeF_2:

$$ClSO_2^- + XeF_2 \rightarrow ClS(O)OXeF_2^- \qquad (4)$$

$$ClS(O)OXeF_2^- \rightarrow ClS(O)OXeF + F^- \qquad (5)$$

$$ClS(O)OXeF \rightarrow SO_2FCl + Xe \qquad (6)$$

It should be noted that such a mechanism would explain the non-appearance of NMe_4SO_2Cl among the products. Also the formation of F^- in reaction (5) would lead logically to the products NMe_4SO_2F and SO_2F_2.

The ability of XeF_2 to function as a Lewis acid is, as yet, unknown, and the above postulated complexes would at best have only a transient existence. SO_2 is known to be a weak Lewis base (complexes with strong Lewis acids such as SbF_5 [5] are relatively unstable) and would not be expected to form an adduct with XeF_2. The addition of the negatively charged fluoride or chloride ion makes the molecule more attractive as a Lewis acid partner and the complex formation with subsequent oxidative decomposition more feasible.

The system $CsF–XeF_2–SO_2$

On condensation of XeF_2 on to a suspension of CsF in SO_2, a finely divided white precipitate formed. At the same time, the caesium fluoride slowly dissolved and a steady gas evolution took place. The solid products isolated from the reaction were $CsSO_3F$, and $CsSO_2F$ when the XeF_2:CsF ratios were less than 2:1. The gaseous products consisted of xenon, SOF_2, SO_2F_2 and trace amounts of $S_2O_5F_2$.

There are obvious differences between the reactions of the caesium fluoride system and the previously discussed tetramethylammonium halide systems. Here SO_3F^- and SOF_2 are major products. The formation of these species in the reaction demands a scheme in which SO_2 undergoes a disproportionation. The dissociation:

$$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-} \qquad (7)$$

has long been discussed. The validity of this proposal has been disputed [6] but isotope-exchange studies have shown that association of SO_2 must take place [7].

The assymetrical breakage of such aggregate molecules with the formation of ionic species, albeit in minimal quantities, is thus feasible. Furthermore, in contrast to the tetramethylammonium salts, caesium fluoride has a low solubility in SO_2. The possibility thus arises that the reaction takes place on the surface of the caesium fluoride and involves complex formation by the fluoride rather than the fluorosulphite ion.

The following steps are proposed:

$$XeF_2 + F^- \rightarrow \text{“}XeF_3^-\text{”} \qquad (8)$$

$$SO^{2+} + XeF_3^- \rightarrow SOF^+ + XeF_2 \qquad (9)$$

$$SOF^+ + XeF_2 \rightarrow SOF_2 + XeF^+ \qquad (10)$$

$$XeF^+ + SO_3^{2-} \rightarrow \text{“}FXeOSO_2^-\text{”} \rightarrow SO_3F^- + Xe \qquad (11)$$

The formation of a transitory species XeF_3^- is to be preferred to other possible mechanisms whereby XeF_2 itself reacts with the SO^{2+} species, *i.e.*

$$SO^{2+} + XeF_2 \rightarrow SOF^+ + XeF^+ \qquad (12)$$

followed by

$$XeF^+ + SO_3^{2-} \rightarrow SO_3F^- + Xe \qquad (13)$$

or

$$SOF^+ + F^- \text{ (from CsF)} \rightarrow SOF_2 \qquad (14)$$

Reaction (12) could also occur in an SO_2 solution of XeF_2 in the absence of additional fluoride ions, and would with certainty lead to irreversible decomposition of the components *via* reaction (13). Such solutions however are stable.

Although the proposed scheme demands equimolar amounts of XeF_2 and CsF, at least a twofold excess of XeF_2 was necessary to form $CsSO_3F$ uncontaminated with $CsSO_2F$, and in all reactions large amounts of SO_2F_2 were also formed. Various possibilities are available to explain the formation of these products. The oxidation of SO_2 by XeF^+ as observed by Bartlett and Sladky [1] and the mechanism discussed under the reactions of NMe_4^+ halides (reaction of SO_2F^- from the small amount of dissolved CsF) are two obvious pathways. The availability of a further route is indicated by the traces of $S_2O_5F_2$ isolated in the products. This could be formed during a further intermediate step in the reaction scheme involving transient combination of XeF^+ and SO_3F^- to form $FXeSO_3F$ followed by reaction with the solvent:

$$FXeSO_3F + SO_2 \rightarrow S_2O_5F_2 + Xe \qquad (15)$$

$FXeSO_3F$ and its decomposition with SO_2 have already been described [8]. That larger amounts of $S_2O_5F_2$ are not formed is understandable when the observations [9 - 11] that $S_2O_5F_2$ reacts with fluoride and fluorosulphite in the following manner are considered:

$$S_2O_5F_2 + F^- \rightarrow SO_2F_2 + SO_3F^- \qquad (16)$$

$$S_2O_5F_2 + SO_2F^- \rightarrow SO_2F_2 + SO_3F^- + SO_2 \qquad (17)$$

A larger XeF_2:CsF ratio would be expected to result in the formation of larger amounts of $FXeSO_3F$, and subsequently $S_2O_5F_2$ and SO_3F^-, whilst at the same time decreasing the yield of SO_2F^- in agreement with the observations.

The system CsCl–XeF_2–SO_2

On gently warming a suspension of CsCl in an SO_2 solution of XeF_2, a similar reaction to that of CsF was observed. Although during the reaction CsCl was seen to dissolve, a twofold excess of XeF_2 was insufficient to cause complete reaction. The products of the reaction were $CsSO_3F$, $CsSO_2F$, SO_2F_2, SO_2FCl and xenon, smaller amounts of SOF_2 and traces of $S_2O_5F_2$.

In spite of the absence of SOFCl among the products, the mechanism proposed for the reaction of CsF with XeF_2 and SO_2 can be applied with success here. The reaction scheme thus becomes:

$$XeF_2 + Cl^- \rightarrow \text{“}XeF_2Cl^-\text{”} \quad (18)$$

$$XeF_2Cl^- + SO^{2+} \rightarrow SOCl^+ + XeF_2 \quad (19)$$

$$SOCl^+ + XeF_2 \rightarrow SOFCl + XeF^+ \quad (20)$$

$$XeF^+ + SO_3^{2-} \rightarrow SO_3F^- + Xe \quad (21)$$

Compared with SO_2F_2 and SO_2FCl, SOFCl is known to be an unstable molecule, disproportionating easily to SOF_2 and $SOCl_2$ [12]. It is hardly surprising, therefore, that in the presence of reactive species such as $S_2O_5F_2$, SO_2F^- and (presumably) $FXeSO_3F$ it should react further. Reasonable reactions would be:

$$S_2O_5F_2 + SOFCl \rightarrow SO_2FCl + SO_2F_2 + SO_2 \quad (22)$$

$$FXeSO_3F + SOFCl \rightarrow SO_2FCl + SO_2F_2 + Xe \quad (23)$$

$$SO_2F^- + SOFCl \rightarrow SOF_2 + SO_2Cl^- \quad (24)$$

A pathway leading to the formation of SO_2F^- but not SO_2Cl^- salts has already been discussed in the related NMe_4Cl system. Of note is the fact that whereas a 2:1 excess of XeF_2 was sufficient to prevent $CsSO_2F$ formation in the reaction with CsF, large quantities were formed under similar conditions in the CsCl reaction. Presumably SOFCl reacts with $S_2O_5F_2$ or some other reactive species preferably to form SO_2F^-.

The formation of SOF_2 during the reaction can be explained either by reaction of the SOF^+ species with fluoride ions set free by an intermediate xenon complex [reaction (5)] or by the already mentioned disproportionation of SOFCl. $SOCl_2$ thus formed could react further with reactive compounds such as SO_2F^- (already observed by Seel and Riehl [4]), $S_2O_5F_2$ or $FXeSO_3F$ forming SO_2FCl in reactions parallel to (22) or (23).

The system KF–XeF_2–SO_2

This system appears to react in an identical manner to the related CsF system. At room temperature no reaction takes place. Products were only isolated after heating for several hours at 100 °C. The lesser reactivity of KF is to be expected when the greater lattice energy of this compound is considered.

Experimental

All starting materials were obtained commercially or prepared using known methods. The halides were heated *in vacuo* and SO_2 was distilled over P_2O_5 before use. Reactions were carried out in a glass/Teflon high-vacuum apparatus.

In a typical experiment, *ca.* 5 cm^3 SO_2 was distilled on to a weighed amount (0.3 - 0.5 g) of halide followed by the desired amount of XeF_2. Following reaction, the volatiles were pumped off. Partial separation of the gaseous products was achieved by fractionation through traps at — 78 °C, —122 °C and —196 °C.

Products were identified by their IR spectra all of which were already known [13 - 18].

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